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(54) Title: POLYMERIZATION CATALYSTS AND PROCESSES THEREFOR (57) Abstract Novel catalyst systems which comprise diimine nickel(0) complexes can be used with methylaluminoxane in slurry polymerization processes to polymerize ethylene and, optionally a higher alpha-olefin comonomer, to produce high molecular weight polymers.		

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POLYMERIZATION CATALYSTS AND PROCESSES THEREFORBACKGROUND

This invention relates to homopolymerization of mono-1-olefin monomers, such as ethylene, and copolymerization of a mono-1-olefin monomer, such as ethylene, with at least one higher alpha-olefin comonomer.

It is well known that mono-1-olefins, such as ethylene, can be polymerized with catalyst systems employing transition metals such as titanium, vanadium, chromium, nickel and/or other metals, either unsupported or on a support such as alumina, silica, titania, and other refractory metals. Supported polymerization catalyst systems are frequently used with a cocatalyst, such as alkyl boron and/or alkyl aluminum compounds. Organometallic catalyst systems, i.e., Ziegler-Natta-type catalyst systems usually are unsupported and frequently are used with a cocatalyst, such as methylaluminoxane.

It is also well-known that, while no polymer production process is easy, slurry, or loop, polymerization processes are relatively much more commercially desirable than other polymerization processes. Furthermore, the type of polymerization process used can have an effect on the resultant polymer. For example, higher reactor temperatures can result in low catalyst activity and productivity, as well as a lower molecular weight polymer product. Higher reactor pressures also can decrease the amount of desirable branching in the resultant polymer.

Most polymer products made in slurry processes, especially those polymer products made using supported chromium catalyst systems, have a broader molecular weight distribution and, therefore, the polymer product is much easier to process into a final product. Polymers made by other processes, such as, for example, higher temperature and/or higher pressure solution processes, can produce polymers having a narrow molecular weight distribution; these polymers can be much more difficult to process into an article of manufacture.

Unfortunately, many homogeneous organometallic catalyst systems have low activity, high consumption of very costly cocatalysts, like methylaluminoxane (MAO), and can produce low molecular weight polymers with a narrow molecular weight distribution. Furthermore, even though MAO can be

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necessary to produce a polymer with desired characteristics, an excess of MAO can result in decreased catalyst system activity. Additionally, these types of homogeneous catalyst systems preferably are used only in solution or gas phase polymerization processes.

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SUMMARY OF THE INVENTION

It is an object of this invention to provide novel catalyst systems useful for polymerization.

It is another object of this invention to provide an improved polymerization process.

10

It is still another object of this invention to provide catalyst systems which are relatively simple to make, have increased activity and increased productivity.

It is a further object of this invention to provide catalyst systems which have reduced cocatalyst consumption.

15

It is yet another object of this invention to provide homopolymers of ethylene and copolymers of ethylene and higher alpha-olefin(s) that can be processed easily, as indicated by increased branching and a broad molecular weight distribution.

20

It is still another object of this invention to provide homopolymers of ethylene and copolymers of ethylene and higher alpha-olefin that have an increased molecular weight.

25

In accordance with this invention catalyst systems that are useful for polymerizing olefins and processes to make such catalyst systems are provided, wherein said catalyst system comprises diimine nickel(0) complexes and methylaluminoxane.

30

In accordance with another embodiment of this invention, slurry polymerization processes comprising contacting in a reaction zone ethylene, and optionally one or more higher alpha-olefins, with a catalyst system comprising diimine nickel(0) complexes in the presence of methylaluminoxane are provided.

In accordance with yet another embodiment of this invention, homopolymers of ethylene and copolymers of ethylene and higher alpha-olefins which can be characterized as having high molecular weight, increased branching and a

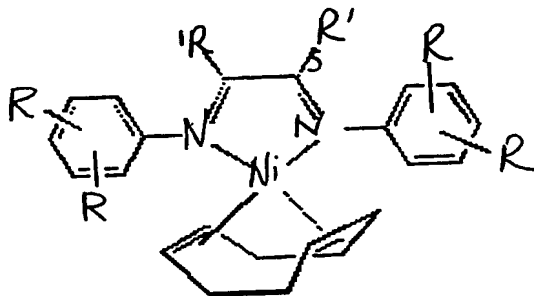
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broad molecular weight distribution, are provided.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Catalyst Systems

Catalyst systems of this invention can be characterized as diimine
5 nickel(0) complexes having a general formula as shown below in Compound I,



Compound I

wherein R can be the same or different and is selected from the
15 group consisting of branched and/or linear alkyl or aromatic groups having from about 1 to about 10, preferably from about 1 to about 8, carbon atoms per alkyl group and R can be in any position on the aromatic ring; and

R' can be the same or different and is selected from the group
consisting of hydrogen and linear, branched, cyclic, bridging, aromatic, and/or
20 aliphatic hydrocarbons, having from about 1 to about 70 carbon atoms per radical group.

R substituents on the aromatic rings of the diimine nickel(0) complex
can be the same or different, and are selected from the group consisting of branched
or linear, aliphatic or aromatic groups having from about 1 to about 8 carbon atoms
25 per alkyl group. Although hydrogen can be used, hydrogen can inhibit synthesis of
the ligand. R groups having more than about 8 carbon atoms per group can result
in a catalyst system with lower activity and/or productivity. While not wishing to
be bound by theory, it is believed that larger substituent groups can cause steric
hindrance in the catalyst system, thereby which can decrease catalyst system activity
and/or productivity. Exemplary alkyl substituents are selected from the group
30 consisting of methyl, ethyl, propyl, isopropyl, butyl, isobutyl, tert-butyl, phenyl
groups, and mixtures of two or more thereof. Preferably, the R substituent is an

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electron-donating species, selected from the group consisting of linear or branched aliphatic groups having from about 1 to about 5 carbon atoms per group. Most preferably, the R groups are both the same and are selected from the group consisting of methyl and isopropyl, due to commercial availability and ease of synthesis of the ligand.

The R group can be in any position, i.e., from 2 to 6, on the aromatic ring. Preferably, the R group, which can be the same or different, is either in the 2 and/or 6 position, due to ease of synthesis. Most preferably, for best catalytic activity and productivity, both R groups are the same and are in the 2 and 6 positions on the aromatic ring.

R' substituents can be the same or different and are selected from the group consisting of hydrogen and branched, linear, cyclic, aromatic or aliphatic radicals having from about 1 to about 70 carbon atoms per radical. Further, the R' substituents can be linked, or joined, across the carbon-carbon bridge between the two nitrogen atoms. While not wishing to be bound by theory, it is believed that radicals having more than 70 carbon atoms can add to the steric hindrance of the catalyst systems and hinder catalyst activity and productivity. Preferably, the R' substituent group is selected from the group consisting of hydrogen and branched, linear, cyclic, aromatic or aliphatic radicals having from about 1 to about 20 carbon atoms per radical, due to commercial availability and ease of synthesis of the ligand. Most preferably, the R' substituent groups are the same or a link across the carbon-carbon bridge between the nitrogen atoms, and the R' substituent is selected from the group consisting of hydrogen and branched, linear, cyclic, aromatic or aliphatic radicals having from about 1 to about 12 carbon atoms per radical, for the reasons given above. Exemplary R' substituents include, but are not limited to, hydrogen, methyl, ethyl, propyl, phenyl, taken together acenaphthyl or cyclobutadienyl. Preferably, the R' substituents are identical and are selected from the group consisting of hydrogen, methyl and acenaphthyl for best resultant catalyst system activity and productivity.

Novel catalyst systems disclosed in this application can be prepared in accordance with any manner known in the art. Preparation of these novel catalyst systems does not require the presence of an oxidizing agent. Most

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preferably, an oxidizing agent is not present, i.e., is absent, during catalyst system preparation. In fact, while not wishing to be bound by theory, it is believed that the presence of an oxidizing agent during catalyst preparation and/or polymerization can be detrimental to either the novel catalyst system and/or the formation of a polymer product because it may cause the formation of an unstable form of the nickel complex that can decompose more easily than the parent nickel complex or the oxidizing agent may react with a cocatalyst to render the cocatalyst unreactive with the nickel complex.

In general, diimine ligands are contacted with a nickel halide to form diimine nickel(0) complexes. Typical syntheses of nickel complexes described in this invention can be found in tom Dieck, H., Svoboda, M., and Greiser, T., Z. Naturforsch B: Anorg. Chem. Organ. Chem., Vol. 36b, pp. 823-832 (1981), herein incorporated by reference. Usually, for ease of catalyst system preparation, the diimine ligand is prepared first. The catalyst preparation procedure can vary, depending on the substituents on the diimine ligand. For example, to prepare a specific diimine ligand, wherein R' is hydrogen, a three-component mixture is prepared. A two-fold molar excess of aniline, containing the desired R substituents ($R_nC_6H_{(7-n)}N$, wherein $n = 1,2$), is contacted with a dialdehyde, such as, for example, glyoxal (CHOCHO), in the presence of a compound capable of being a solvent for both organic and aqueous compounds. Exemplary solvents for both organic and aqueous compounds include, but are not limited to, methanol, ethanol and/or tetrahydrofuran (THF). The mixture can be contacted, preferably refluxed, under any atmosphere to form the desired ligand. Preferably, the mixture is refluxed for at least 10, preferably 20 minutes, cooled and the desired ligand can be recovered. Generally, after refluxing and cooling, the ligand can be recovered in a crystalline form.

To prepare another specific diimine ligand wherein the R' group is anything other than hydrogen, a similar procedure can be used. For example, at least a two-fold molar excess of aniline or a substituted aniline can be combined with a compound capable of dissolving both organic and aqueous compounds and a very minor amount of formic acid. Then, about a one molar equivalent of an alpha-diketone ($R'COCOR'$) can be added to the mixture. The mixture can be stirred,

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under atmospheric conditions of temperature and pressure until the reaction is complete and the desired ligand is formed. Preferably, water is absent from the reaction mixture. Generally, the reaction will be complete in about 18, preferably 24 hours. A crystalline ligand product can be recovered according to any method
5 known in the art.

The diimine nickel(0) catalyst system complex can be prepared, again by any method known in the art. For example, approximate molar equivalents of a diimine ligand and a nickel(0) can be contacted in the presence of any compound that can dissolve both the diimine ligand and nickel(0), either partially or
10 completely. The contacting conditions can be any conditions suitable to effect the formation of a diimine nickel(0). Preferably, for best product results, the diimine ligand/nickel(0) mixture is contacted at room temperature under a dry atmosphere for any amount of time sufficient to form the diimine nickel(0) compound. Completion of the formation of the diimine nickel(0) complex can be evidenced by
15 a color change. Generally, contacting times of about 8, and preferably 12 hours are sufficient. Usually, as a result of the preparation procedure, the resultant diimine nickel(0) will comprise from about 3 to about 20, preferably from about 5 to about 15, weight percent nickel, based on the total mass of the diimine nickel(0). The presence of oxygen is not thought to be detrimental to this aspect of the preparation
20 procedure.

After formation of a diimine nickel(0), the diimine nickel(0) can be recovered by any method known in the art, such as, for example evaporation and/or vacuum filtration of the solvent. Further, if desired, the diimine nickel(0) can be further purified by washing. One exemplary wash compound can be heptane. The
25 diimine nickel(0) catalyst system can be recovered and used as a solid, heterogeneous catalyst system.

Reactants, Polymerization and Polymer Products

Polymers produced according to the process of this invention can be homopolymers of ethylene or copolymers of ethylene and a higher alpha-olefin. If
30 the reaction product is a copolymer, ethylene can be polymerized with a comonomer which is a higher alpha-olefin having from 3 to about 8 carbon atoms per molecule. Exemplary comonomers include, but are not limited to, propylene, 1-butene, 1-

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pentene, 1-hexene, 1-octene, 4-methyl-1-pentene, and mixtures thereof. Preferably, the comonomer is 1-hexene and/or 4-methyl-1-pentene, in order to achieve maximum polymer product toughness.

If a comonomer is used, the comonomer can be added to the polymerization reactor, or reaction zone, in an amount within a range of about 1 to about 20 weight percent, preferably within 7 to about 18 weight percent, based on the weight of the ethylene monomer. Most preferably, a copolymer is present near the reaction zone within a range of about 10 to about 16 weight percent, in order to produce a polymer having the most desired physical properties.

Polymerization of the monomer and comonomer must be carried out under slurry, also known as loop/slurry or particle form, polymerization conditions wherein the temperature is kept below the temperature at which polymer swells significantly. Slurry polymerization processes are much easier to operate and maintain than other polymerization processes; a polymer product produced by a slurry process can be recovered much more easily. Such polymerization techniques are well-known in the art and are disclosed, for instance, in Norwood, U.S. Pat. No. 3,248,179, the disclosure of which is hereby incorporated by reference.

The slurry process generally is carried out in an inert diluent (medium), such as, for example, a paraffin, cycloparaffin, and/or aromatic hydrocarbon. Preferably, the inert diluent is an alkane having less than about 12 carbon atoms per molecule, for best reactor operation and polymer product. Exemplary diluents include, but are not limited to propane, n-butane, isobutane, n-pentane, 2-methylbutane (isopentane), and mixtures thereof. Isobutane is the most preferred diluent due to low cost and ease of use.

The temperature of the polymerization reactor, or reaction zone, when using isobutane as the reactor diluent, according to this invention, is critical and must be kept within a range of about 5° to about 100°C (41° - 212°F) and preferably within a range of about 10° to about 70°C (50° - 158°F). Most preferably, the reaction zone temperature is within a range of 20° to 45°C (68° - 113°F) for best catalyst activity and productivity. Reaction temperatures below about 10°C can be ineffective for polymerization.

Pressures in the slurry process can vary from about 100 to about

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1000 psia (0.76 - 7.6 MPa), preferably from about 200 to about 700 psia. Most preferably, the reaction zone is maintained at a pressure within a range of 300 to 600 psia for best reactor operating parameters and best resultant polymer product. The catalyst system is kept in suspension and is contacted with the monomer and
5 comonomer(s) at sufficient pressure to maintain the medium and at least a portion of the monomer and comonomer(s) in the liquid phase. The medium and temperature are thus selected such that the polymer or copolymer is produced as solid particles and is recovered in that form. Catalyst system concentrations in the reactor can be such that the catalyst system content ranges from 0.001 to about 1
10 weight percent based on the weight of the reactor contents.

The catalyst system and methylaluminoxane (MAO) can be added to the reactor in any order to effect polymerization. For example, catalyst system can be added, then some reactor diluent, such as isobutane, followed by MAO, then more diluent and finally, ethylene. However, as stated earlier, this addition order
15 can be varied, depending on equipment availability and/or desired polymer product properties. Preferably, the catalyst system and MAO are not precontacted prior to addition to the polymerization reactor due to a possible decrease in catalyst activity.

The amount of catalyst system and MAO added to the reactor can vary. Generally, a molar excess of MAO is present, relative to the nickel
20 compound. Preferably, the aluminum to nickel (Al:Ni) molar ratio is less than about 850:1, more preferably within a range of about 50:1 to about 600:1. Most preferably, the molar ratio of aluminum to nickel is within a ratio of 100:1 to 400:1 for best catalyst system activity and productivity.

Two preferred polymerization methods for the slurry process are
25 those employing a loop reactor of the type disclosed in Norwood and those utilizing a plurality of stirred reactors either in series, parallel or combinations thereof wherein the reaction conditions can be the same or different in the different reactors. For instance, in a series of reactors, a chromium catalyst system which has not been subjected to the reduction step can be utilized either before or after the
30 reactor utilizing the catalyst system of this invention.

Polymers produced in accordance with this invention generally have a relatively narrow heterogeneity index (HI), which is a ratio of the weight average

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molecular weight (M_w) and the number average molecular weight (M_n) (also expressed as M_w/M_n). Polymers produced in accordance with this invention usually have a HI within a range of about 3 to about 10, preferably within a range of about 5 to about 8, for best indication of processability.

5 Polymers produced in accordance with this invention are very unique because of a significant amount of short chain branching which can be produced even in the absence of a comonomer added to the reactor. This short chain branching is evidence that some sort of comonomers are produced in-situ in the reactor and are incorporated into the polymer and/or that the catalyst can form
10 short chain branches by rearrangement of the main polymer chain through successive hydride elimination, olefin rotation, and hydride re-addition reactions. Such rearrangements can be termed "chain walking". Chain walking can be described by the active metal catalyst, i.e. nickel, "walking" a distance along the polymer backbone during polymerization and hence, the short chain branch length
15 can be dictated by the rate of ethylene insertion relative to the combined rates of hydride elimination, olefin rotation, and hydride re-addition. Usually polymers produced in accordance with this invention, wherein no comonomer is added to the polymerization reactor comprise up to about 3000, and generally from about 20 to about 3000 short chain branches per 10,000 (or from about 2 to about 300 short
20 chain branches per 1000) backbone carbon atoms of the polymer. Furthermore, the short chain branches produced comprise both odd and even carbon branches, i.e., branches comprising an odd number of carbon atoms per short chain branch, as well as branches comprising an even number of carbon atoms per short chain branch.

 If desired, optional addition of one or more comonomers can be
25 added to the polymerization reactor. The affirmatively added comonomers can further increase the amount of short chain branching in the resultant polymer, or copolymer. Polymers produced with the addition of a comonomer can have a greater number of short chain branches in addition to those generated as described above. If a comonomer is affirmatively added to the polymerization reactor, these
30 polymers usually can comprise up to about 3500, and generally from about 20 to about 3500, short chain branches per 10,000 backbone carbon atoms of polymer.

A further understanding of the invention and its advantages is

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provided by the following examples.

EXAMPLES

The following Examples illustrate various aspects of the invention.

Data are included for each example about the polymerization conditions, as well as
5 the resultant polymer. All chemical handling, including reactions, preparation and
storage, was performed under a dry, inert atmosphere (usually nitrogen). Unless
otherwise indicated, bench scale polymerizations were completed in a 2.6 liter
autoclave reactor at the desired temperature using an isobutane (1.2 liter) slurry.
The reactor was heated to 120°C and purged with nitrogen for about 20 minutes.
10 The reactor then was cooled to the desired polymerization temperature and
pressurized with isobutane to about 400 psig. A known quantity (mass) of diimine
nickel(0) complex catalyst was charged to the reactor against a countercurrent of
isobutane and the agitator was set at 490 rpm. If hydrogen was charged to the
reactor, hydrogen addition was followed by isobutane. The desired quantity of
15 methylaluminoxane (MAO) (10 weight % in toluene) was charged directly to the
reactor via syringe. After the full volume of isobutane was added, ethylene was
added to bring the total reactor pressure to 550 psig. Ethylene was fed on demand
and the polymerization reaction terminated when ethylene flow into the reactor
ceased.

20 The abbreviation for the catalyst systems used is as follows:



N,N'-bis(2,6-diisopropylphenyl)-2,3-butanediimine nickel(0) cyclooctadiene.

In general, catalyst systems used for polymerization in the Examples
were prepared as described in this application.

25 Polymer density was determined in grams per cubic centimeter (g/cc)
on a compression molded sample, cooled at about 15°C per hour, and conditioned
for about 40 hours at room temperature in accordance with ASTM D1505 and
ASTM D1928, procedure C. High load melt index (HLMI, g/10 mins) was
determined in accordance with ASTM D1238 at 190°C with a 21,600 gram weight.
30 Melt index (MI, g/10 mins) was determined in accordance with ASTM D1238 at
190°C with a 2,160 gram weight. Size exclusion chromatography (SEC) analyses
were performed at 140°C on a Waters, model 150 GPC with a refractive index

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detector. A solution concentration of 0.17 to 0.65 weight percent in 1,2,4-trichlorobenzene was found to give reasonable elution times.

Example 1

5 This example shows that high catalyst system activity and productivity can be maintained at commercial reactor temperatures and at low levels of MAO, based on the amount of nickel in the catalyst system.

10 Polymerizations in the following Runs were carried out as described above, with a reactor pressure of 550 psig ethylene in isobutane slurry. MAO was added in a 10% wt/wt solution in toluene. 5 ml of MAO was added in each Run, unless stated otherwise. Polymerization results are listed below in Table 1.

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TABLE I

Run Number	Catalyst	Catalyst Charged (g)	Al:Ni (Molar)	Reactor Temp (°C)	Run Time (Min)	Productivity (g pol/g Ni)	Activity (g pol/g Ni/hr)
101	$[(iPr_2Ph)_2DABMe_2]Ni(COD)$	0.0058	838	40	18	47001	156,670
102	$[(iPr_2Ph)_2DABMe_2]Ni(COD)$	0.0104	467	60	88	18724	12,770
103	$[(iPr_2Ph)_2DABMe_2]Ni(COD)$	0.0181	268	80	2.5	4303	103,270

5

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The data in Table 1 show that diimine nickel(0) catalyst systems can effectively polymerize ethylene with low Al:Ni molar ratios, i.e., less than about 850, and even less than about 500. Catalyst productivities, with these low Al:Ni molar ratios, still can be very high, usually higher than 15,000 grams polymer per gram nickel and even up to greater than 45,000 grams polymer per gram nickel. Also note that the reactor temperatures are within commercially acceptable ranges, i.e., between 40 and 80°C.

Example 2

This example shows that high polymer branching can be retained at high reactor pressures and temperatures. Branching numbers in Table 2 were determined in accordance with standard infrared (IR) procedures, using the 1378 cm⁻¹ asymmetric stretching band. Again, all of the following polymerizations were carried out as described above, with a reactor pressure of 550 psig ethylene in isobutane slurry. MAO was added in a 10% wt/wt solution in toluene. Five (5) ml of MAO was added in each Run, unless stated otherwise. Polymerization catalyst systems and results are listed below in Table 2.

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Table 2

Run	Catalyst	Catalyst Charged (g)	Al:Ni (molar ratio)	Reactor Temp (°C)	Run Time (min)	Productivity (g pol/g Ni)	Density (g/cc)	Branch Methyls
201	$[(^i\text{Pr}_2\text{Ph})_2\text{DABMe}_2]\text{Ni}(\text{COD})$	0.0058	838	40	18	47001	0.911	155
202	$[(^i\text{Pr}_2\text{Ph})_2\text{DABMe}_2]\text{Ni}(\text{COD})$	0.0104	467	60	8	18724	0.908	29
203	$[(^i\text{Pr}_2\text{Ph})_2\text{DABMe}_2]\text{Ni}(\text{COD})$	0.0181	268	80	2.5	4303	0.880	256

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The extent of branching determined by IR methods is shown in Table 2. The number of branch methyls shown in Table 2 has been adjusted to exclude polymer end-group methyls, i.e., terminal methyls of a polymer chain. High amounts of branching are evident at all pressures and temperatures.

5

Example 3

This example shows that polymers having a broader molecular weight distribution can be produced with the inventive catalyst systems using the inventive polymerization process. All Runs were performed at 550 psig and at temperatures between 27° and 80°C. The amount of MAO in toluene solution added was 5 ml for all Runs. The results are given in Table 3.

10

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Table 3

Run	Catalyst	Catalyst Charged (g)	Al:Ni (molar ratio)	Reactor Temp (°C)	Run Time (min)	Productivity (g pol/g Ni)	Mw	Mn	HI (Mw/Mn)
401	$[(\text{Pr}_2\text{Ph})_2\text{DABMe}_2]\text{Ni}(\text{COD})$	0.0165	295	27	30	28909	2065	261	7.9
402	$[(\text{Pr}_2\text{Ph})_2\text{DABMe}_2]\text{Ni}(\text{COD})$	0.0136	357	27	34	44167	2215	416	5.3
403	$[(\text{Pr}_2\text{Ph})_2\text{DABMe}_2]\text{Ni}(\text{COD})$	0.0058	838	40	18	47001	2290	642	3.6
404	$[(\text{Pr}_2\text{Ph})_2\text{DABMe}_2]\text{Ni}(\text{COD})$	0.0104	467	60	88	18724	1853	619	3.0
405	$[(\text{Pr}_2\text{Ph})_2\text{DABMe}_2]\text{Ni}(\text{COD})$	0.0181	268	80	2.5	4303	479	133	3.6

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The data in Table 3 show that a relatively broad molecular weight distribution, as evidenced by the heterogeneity index (HI) which is a ratio of M_w/M_n , can be achieved for an ethylene polymer produced with a diimine nickel(0) catalyst system at any reactor temperature and pressure, as well as low Al:Ni molar ratios.

While this invention has been described in detail for the purpose of illustration, it is not to be construed as limited thereby but is intended to cover all changes and modifications within the spirit and scope thereof.

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CLAIMS

1. A polymerization process comprising contacting in a reaction zone under slurry polymerization reactor conditions:

a) ethylene and

b) a heterogenous catalyst system comprising methylaluminumoxane and one or more diimine nickel(0) complexes;

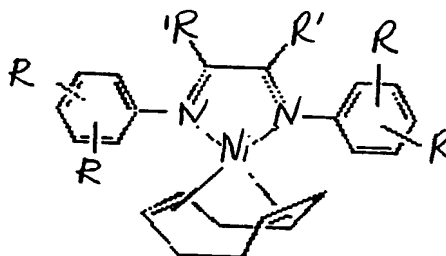
wherein a polymer is recovered.

2. A process according to claim 1, further comprising a comonomer selected from the group of alpha-olefins having from 3 to 10 carbon atoms per molecule is present.

3. A process according to claim 2, wherein said comonomer is selected from the group consisting of propylene, 1-butene, 1-pentene, 1-hexene, 1-octene, 4-methyl-1-pentene, and mixtures thereof.

4. A process according to claim 3, wherein said comonomer is selected from the group consisting of 1-hexene, 4-methyl-1-pentene, and mixtures thereof.

5. A process according to claim 1, wherein said diimine nickel(0) complex is represented by the formula



wherein R can be the same or different and is selected from the group consisting of branched and/or linear alkyl or aromatic groups having from about 1 to about 10 carbon atoms per alkyl group and can be in any position on the aromatic ring; and

R' can be the same or different and is selected from the group consisting of hydrogen and linear, branched, cyclic, bridging, aromatic, and/or aliphatic hydrocarbons, having from about 1 to about 70 carbon atoms per radical group.

6. A process according to claim 5, wherein said R substituent is selected from the group consisting of linear or branched aliphatic groups having from about 1 to about 8 carbon atoms per group.

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7. A process according to claim 6, wherein said R substituent is selected from the group consisting of methyl groups, isopropyl groups, and mixtures thereof.

8. A process according to claim 5, wherein said R' substituent is selected from the group consisting of hydrogen and branched, linear, cyclic, aromatic or aliphatic radicals having from about 1 to about 12 carbon atoms per radical.

9. A process according to claim 8, wherein said R' substituent is selected from the group consisting of hydrogen, methyl groups, ethyl groups, propyl groups, phenyl groups, acenaphthyl groups, cyclobutadienyl groups or mixtures thereof.

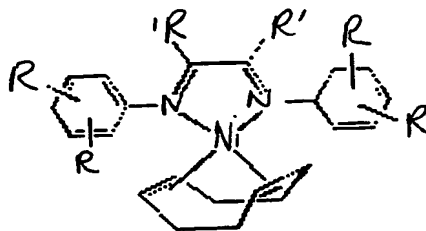
10. A process according to claim 1, wherein said diimine nickel(0) complexes and said methylaluminoxane are present in the reactor in amounts to have an aluminum to nickel molar ratio of less than about 850:1.

11. A process according to claim 10, where in said aluminum to nickel molar ratio is within a range of about 50:1 to about 600:1.

12. A process according to claim 1, wherein said slurry polymerization reactor conditions comprise a temperature within a range of about 10° to about 90°C and a pressure within a range of about 100 to about 1000 psia.

13. A process according to claim 1, wherein said slurry polymerization reactor conditions comprise a diluent of isobutane.

14. A heterogeneous catalyst composition comprising:
a) diimine nickel(0) complexes having the formula of



wherein R can be the same or different and is selected from the group consisting of branched and/or linear alkyl or aromatic groups having from about 1 to about 10 carbon atoms per alkyl group and can be in any position on the aromatic ring; and

R' can be the same or different and is selected from the group

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consisting of hydrogen and linear, branched, cyclic, bridging, aromatic, and/or aliphatic hydrocarbons, having from about 1 to about 12 carbon atoms per radical group and

b) methylaluminoxane.

5 15. A composition according to claim 14, wherein said R substituent is selected from the group consisting of linear or branched aliphatic groups having from about 1 to about 8 carbon atoms per group.

16. A composition according to claim 15, wherein said R substituent is selected from the group consisting of methyl groups, isopropyl groups, and mixtures thereof.

10 17. A composition according to claim 14, wherein said R' substituent is selected from the group consisting of hydrogen and branched, linear, cyclic, aromatic or aliphatic radicals having from about 1 to about 12 carbon atoms per radical.

15 18. A composition according to claim 17, wherein said R' substituent is selected from the group consisting of hydrogen, methyl groups, ethyl groups, propyl groups, phenyl groups, acenaphthyl groups, cyclobutadienyl groups or mixtures thereof.

19. A composition according to claim 14, wherein said diimine nickel(0) complexes and said methylaluminoxane are present in an amount to have an aluminum to nickel molar ratio of less than about 850:1.

20 20. A composition according to claim 19, wherein said aluminum to nickel molar ratio is within a range of about 50:1 to about 600:1.

21. A polymer composition of ethylene comprising from 20 to 3000 short chain branches per 10,000 backbone carbon atoms of said polymer and
25 wherein said polymer has a heterogeneity index in the range of about 3 to about 10.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/08663

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08F10/00 C08F4/70

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	WO 96 23010 A (DU PONT ; UNIV NORTH CAROLINA (US)) 1 August 1996 see claims; page 78, compound no. XXXIII; page 138, lines 17-32; page 288, example 252 --- -/--	1-21



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/08663

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Information on patent family members

National Application No

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